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CONTENTS

- P. ZEEMAN and J. DE GIER: "Third preliminary note on some experiments concerning the isotope of hydrogen", p. 2. (With one plate).
- A. A. NIJLAND: "Mittlere Lichtkurven von langperiodischen Veränderlichen. XVII. S Coronae borealis", p. 3. (With one plate).
- F. M. JAEGER and J. A. VAN DIJK: "On Complex Salts with α - α' -Dipyridyl: Complex Salts of bivalent Nickel", p. 10.
- J. PIÉRAND: "Détermination des Intensités Relatives des Composantes du Multiplet $a^3F-y^3F^0$ de $Fe I$ ". (Communicated by Prof. L. S. ORNSTEIN), p. 16.
- EVERT GORTER: "The lyotropic series and the spreading of proteins". (Communicated by Prof. J. VAN DER HOEVE), p. 20.
- G. G. LOUMAN: "On the occurrence of Interglacial (Risz-Würm) Peat in Holland". (Communicated by Prof. H. A. BROUWER), p. 22.
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Physics. — *Third preliminary note on some experiments concerning the isotope of hydrogen.* By P. ZEEMAN and J. DE GIER.

(Communicated at the meeting of December 16, 1933.)

Exhibition of the mass defect.

We shall now proceed to show how the method of J. J. THOMSON's parabolas gives valuable results with a mixture of *He* and hydrogen, containing 10 % of the heavy isotope. We have already announced ¹⁾ that it was possible to exhibit the mass differences between *He* and $H_2^1 H^2$, $He H^1$ and $H^1 H_2^2$, $He H^{2+}$ and H_3^{2+} . The mass defects are most beautifully exhibited in some photographs, annexed to the present communication. The amount of the defect can be measured with some accuracy ²⁾.

The parabolas to be compared must not differ too much in intensity and at the same time they should be as narrow as possible. These conditions cannot be fulfilled at the same time for the three doublets mentioned.

When the doublet 5 appears well defined the doublet 4 is strongly superposed and not resolved.

Fig. 1a of the plate gives the original photograph in twofold magnification with the doublet 4, and Fig. 1b part of the photograph in eightfold enlargement.

Fig. 2a and Fig. 2b give corresponding photographs for doublet 5.

The photographs were measured by a comparator and the mass difference calculated by means of THOMSON's interpolation formula

$$\frac{1}{\sqrt{m_3}} = \frac{y_3 - y_1}{y_2 - y_1} \left(\frac{1}{\sqrt{m_2}} - \frac{1}{\sqrt{m_1}} \right) + \frac{1}{\sqrt{m_1}}.$$

The results differ only by 1 or 1.5 % from the difference we deduce from BAINBRIDGE's data ³⁾.

In order to obtain the best results from the photographs it will be necessary to use a calibration curve as first indicated by Aston. It appears however that the theoretical formula gives rather accurate results.

For the study of the mass defects of the heavier ions the parabolas are to be refined still further. On some of our photographs we obtained a nearly complete record of *OH* combinations including $OH^1 H_2^2 = 21$.

¹⁾ ZEEMAN and DE GIER. Proceedings Amsterdam. Vol. 36. N^o. 7, p. 717. 1933 being the continuation of a paper in the same Proceedings p. 609, communicated June 24, 1933.

²⁾ A doublet for H_2^{1+} and He^{++} is already given by LUKANÓW and SCHÜTTE. Zs. f. Physik 82, 600. 1933.

³⁾ K. T. BAINBRIDGE. Phys. Rev. July 1933. 56, 57.

P. ZEEMAN AND J. DE GIER: THIRD PRELIMINARY NOTE ON SOME
EXPERIMENTS CONCERNING THE ISOTOPE OF HYDROGEN.

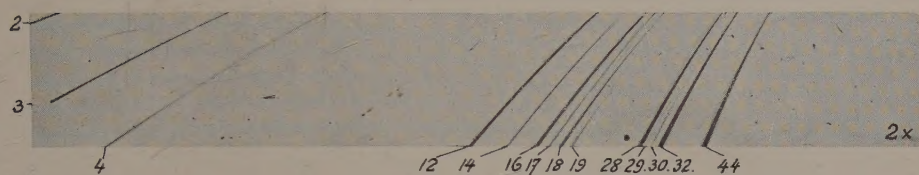


Fig. 1a

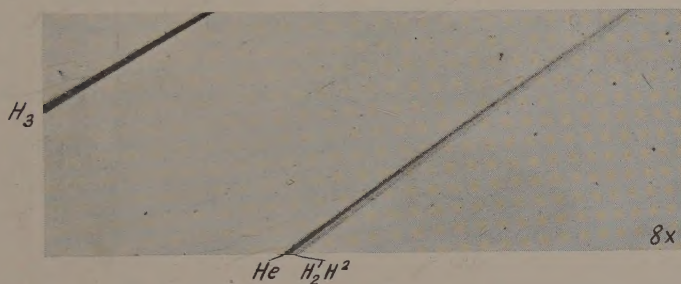


Fig. 1b

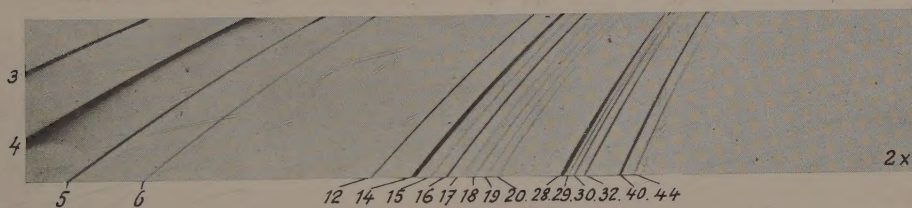


Fig. 2a

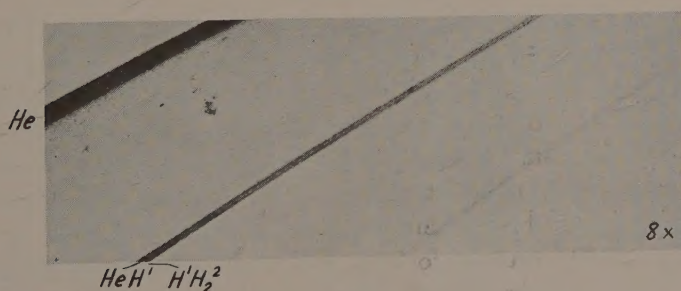


Fig. 2b

It is to be regretted that the hydrogen used contained some traces of Ar so that $O H_2^1 H^2$ coincides with Ar^{++} .

On the other hand the contamination with argon gives a parabola $\frac{m}{e} = 42 \text{ } Ar H^2$ as is to be expected from the explanation that $\frac{m}{e} = 41$ corresponds to $Ar H^1$ and not to an isotope of Ar^1).

We are now experimenting with concentrated Ne in order to solve the problem hydride-isotope for the line corresponding to an element with an atomic weight 23.

The heavy isotope of hydrogen obtained directly from water vapour.

Finally we have to record an experiment made with hydrogen obtained by conducting a stream of the vapour of distilled water over sodium. The photograph showed a faint parabola with $\frac{m}{e} = 4$, the time of exposition being half an hour. With a very small addition of helium it became possible to determine an accurate value of the H isotope, without any previous concentration of the isotope.

¹⁾ P. ZEEMAN and J. DE GIER, Amsterdam, Proceedings 36, 609, note 4a.

Astronomy. — Mittlere Lichtkurven von langperiodischen Veränderlichen. XVII. *S Coronae borealis*. Von A. A. NIJLAND.

(Communicated at the meeting of December 16, 1933.)

Instrumente *S* und *R*. Die Beobachtungen wurden alle auf *R* reduziert; die Reduktion *R*—*S* beträgt $-0^m.19$. Spektrum M6—8e (HA 79, 174). Gesamtzahl der Beobachtungen 742 (von 2417317 bis 2427410). Es wurden wieder, wie in allen früheren Mitteilungen, die in zwei Instrumenten angestellten Schätzungen nur einmal gezählt.

Es wurden zwei stark abweichende Schätzungen (2421793 und 6449) verworfen. Einschliesslich der Beobachtung 9695 (*S* unsichtbar) zählten also drei Beobachtungen nicht mit, und es bleiben 739 Schätzungen für die Diskussion übrig.

Karte: HAGEN, *Atlas Stell. var. Series III*.

Die Tabelle I giebt eine Übersicht der benutzten Vergleichsterne. Das Spektrum der neunten Spalte wurde den HA 96 entnommen; die hier für die Sterne *C*, *B*, *A*, *b* und *c* gegebenen Helligkeiten sind mit denjenigen aus HA 37 identisch. Wiederholt wurde auch der Veränderliche *U Cor. bor.* im vollen Lichte als Vergleichstern herangezogen. Aber auch Schätzungen wie *A 7 S 5 U 2 b* (9133.571, *U* in Zunahme begriffen) fanden in

TABELLE I. Vergleichsterne.

	BD	HAGEN	St.	PD	PD <i>red.</i>	HA 29	HA 37	Sp.	<i>H</i>
<i>C</i>	+ 30.°2647	—	78.4	^m 5.78 WG	^m 5.69	—	^m 5.57	K 0	^m 5.33
<i>B</i>	+ 33.2574	—	69.1	6.62 W+	6.31	—	6.14	A 2	6.28
<i>A</i>	+ 31.2724	2	63.8	7.20 GW	6.67	^m 6.81	6.86	F 5	6.83
<i>U</i>	+ 32.2569	3	56.1	—	—	—	—	B 8	7.62
<i>b</i>	+ 32.2578	4	52.5	—	HA 74	7.87	7.91	F 0	7.98
<i>c</i>	+ 32.2577	5	47.5	—	^m 8.67	8.48	8.54	F 8	8.50
<i>d</i>	+ 32.2572	6	42.7	—	8.93	8.95	—	—	8.99
<i>e</i>	+ 31.2723	9	39.0	—	—	9.35	9.42	—	9.37
<i>f</i>	+ 31.2726	10	30.7	—	—	10.59	[10.65]	—	10.22
<i>g</i>	—	—	26.6	Grenze	—	—	—	—	10.64
<i>h</i>	—	—	21.8	^m 11.21	—	—	—	—	11.13
<i>k</i>	—	14	15.5	—	—	—	11.68	—	11.76
<i>l</i>	—	18	9.6	—	—	—	12.36	—	12.38
<i>m</i>	—	20	6.9	—	—	—	—	—	12.65
<i>p</i>	—	29	0 0	—	—	—	—	—	13.36

der Form *A 7 S 7 b* Verwendung; s. übrigens AN 5727. Dass die dort angenommenen Helligkeiten für die Sterne *A*, *b*, *c* und *d* (und für *U* im vollen Lichte) von den hier gegebenen etwas abweichen, war zu erwarten, da sich die beiden Bearbeitungen auf verschiedenem Material stützen.

Koordinaten der Sterne *g* und *h*:

$$\left. \begin{array}{l} g: \alpha = 15^{\text{h}} 15^{\text{m}.4} \quad \delta = +31^{\circ}25' \\ h \quad \quad \quad 15 \quad .4 \quad \quad \quad 41 \end{array} \right\} (1900).$$

Stern *h* wurde 5-mal (2418032, 2420697, 0751 2-mal, 7309) an die Grenze von *S* angeschlossen. Das untere Ende der Stufenskala ist unsicher, da hier keine Vergleichsterne vorliegen. Die Stufenskala bezieht sich auf die Helligkeit $10^{\text{m}.0}$; der Stufenwert ist $0^{\text{m}.102}$. Der Anschluss an die photometrischen Helligkeiten ist mit Ausnahme der Sterne *C* und *f* sehr befriedigend.

Es liegen 69 Schätzungen der Farbe vor, welche für drei Viertel aus den Jahren 1906 bis 1921 stammen (Tabellen IIa und IIb).

Die Farbauffassung ist im Laufe der Jahre scheinbar ziemlich konstant geblieben. Eine Abhängigkeit der Farbe von der Helligkeit ist aber diesmal unverkennbar; von 6^{m} bis 9^{m} vertieft die Farbe sich von $3^{\circ}.3$ bis $4^{\circ}.3$. Das allgemeine Mittel ist $3^{\circ}.72$.

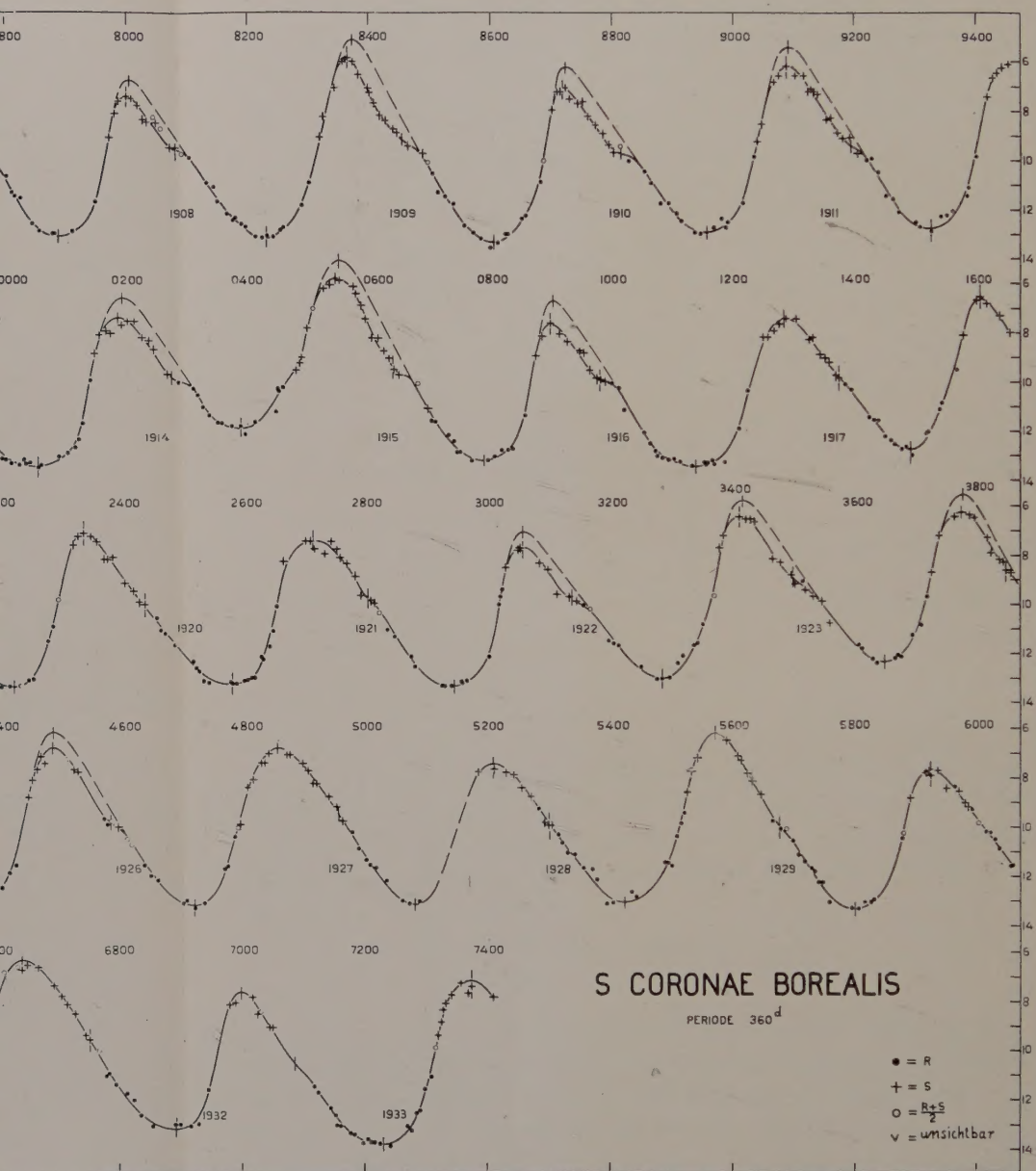


Fig. 1.

TABELLEN IIa und IIb. Farbenschätzungen.

Zeitraum	<i>n</i>	Farbe	Grösse	<i>n</i>	Farbe
2417324 — 8363	21	^c 3.45	^m 6.21	12	^c 3.21
8373 — 9846	21	3.79	6.54	12	3.42
2420203 — 4509	19	3.63	7.00	12	3.62
5201 — 6640	8	4.62	7.45	12	4.00
	69		8.06	12	3.88
			9.37	9	4.33
				69	

Die Figur 1 enthält die Beobachtungen, alle auf *R* reduziert ¹⁾. Die Reihe der Abweichungen (Beobachtung minus Kurve) zeigt 269 Plus-, 294 Minuszeichen, 179 Nullwerte, 265 Zeichenfolgen, 297 Zeichenwechsel. Das Mittel der absoluten Werte der Abweichungen ist 0^m.118.

Ein Einfluss des Mondscheines auf die Helligkeitsschätzung ist kaum bemerkbar. Es verteilen sich auf 244 bei Mondschein angestellte Beobachtungen die Abweichungen wie folgt: 103 Plus-, 85 Minuszeichen, 56 Nullwerte.

Die Tabelle III enthält die aus der Kurve abgelesenen Epochen der Minima *m* und der Maxima *M*, nebst einer Vergleichung mit den einfachen Elementen *R*:

$$\begin{aligned} &2422207^d + 360^d E \text{ (für die Minima)} \\ \text{und} &2422334 + 360 E \text{ (für die Maxima).} \end{aligned}$$

Das Maximum 7374, das erst nach Ablauf der Reduktion bestimmt wurde, blieb hier ausser Acht. Die Reihe der übrigbleibenden *B—R* zeigt einen Überschuss von Zeichenfolgen, und es wird für die beiden Hauptphasen eine wesentliche Verbesserung durch die Hinzuziehung eines — graphisch abgeleiteten — periodischen Gliedes erzielt.

Die definitiven Elemente *F* lauten:

$$\left. \begin{array}{l} 2422207^d \\ 2422334 \end{array} \right\} + 360^d E + 10^d \sin 15^\circ (E + 8).$$

Diese Elemente stimmen leidlich gut mit den früher von CHANDLER abgeleiteten (MNRAS 80, 286):

$$2400647^d + 361^d.1 E' + 8^d \sin (12^\circ E' + 327^\circ)$$

oder, für $E' = E + 60$:

$$2422313^d + 361^d.1 E + 8^d \sin 12^\circ (E + 27)$$

überein. Nach der *G und L* (II, 10) war die Periode bis 1915 recht konstant

¹⁾ Die Schätzung 3558 (*S* = 10^m.8) wurde nicht im Sucher angestellt.

TABELLE III.

<i>E</i>	Minima <i>m</i>					Maxima <i>M</i>				
	<i>B</i>	<i>v</i>	<i>R</i>	<i>B-R</i>	<i>B-F</i>	<i>B</i>	<i>v</i>	<i>R</i>	<i>B-R</i>	<i>B-F</i>
— 13	—	—	—	—	—	²⁴¹ 7643	^m 6.3	7654	— 11	— 1
— 12	²⁴¹ 7891	^m 13.0 ⁵	7887	+ 4	+ 13	8000	7.3 ⁵	8014	— 14	— 5
— 11	8234	13.1	8247	— 13	— 6	8366	5.8	8374	— 8	— 1
— 10	8607	13.3	8607	0	+ 5	8720	7.0 ⁵	8734	— 14	— 9
— 9	8956	12.9	8967	— 11	— 8	9088	6.2	9094	— 6	— 3
— 8	9326	12.8	9327	— 1	— 1	9450	6.1	9454	— 4	— 4
— 7	9698	13.5	9687	+ 11	+ 8	9824	7.2	9814	+ 10	+ 7
— 6	²⁴² 0060	13.4	0047	+ 13	+ 8	²⁴² 0188	7.3 ⁵	0174	+ 14	+ 9
— 5	0393	11.8	0407	— 14	— 21	0546	5.8	0534	+ 12	+ 5
— 4	0792	13.2	0767	+ 25	+ 16	0899	7.7	0894	+ 5	— 4
— 3	1138	13.4	1127	+ 11	+ 1	1283	7.4	1254	+ 29	+ 19
— 2	1492	12.7	1487	+ 5	— 5	1607	6.6	1614	— 7	— 17
— 1	1851	12.2	1847	+ 4	— 6	1985	5.9	1974	+ 11	+ 1
0	2225	13.3	2207	+ 18	+ 9	2335	7.0	2334	+ 1	— 8
+ 1	2581	13.1	2567	+ 14	+ 7	2712	7.3 ⁵	2694	+ 18	+ 11
+ 2	2944	13.2	2927	+ 17	+ 12	3055	7.6	3054	+ 1	— 4
+ 3	3284	13.0	3287	— 3	— 6	3409	6.4	3414	— 5	— 8
+ 4	3648	12.3	3647	+ 1	+ 1	3775	6.2	3774	+ 1	+ 1
+ 5	4002	12.6	4007	— 5	— 2	4124	6.3	4134	— 10	— 7
+ 6	4363	13.1	4367	— 4	+ 1	4487	6.7	4494	— 7	— 2
+ 7	4720	13.1	4727	— 7	0	4855	6.7	4854	+ 1	+ 8
+ 8	5082	13.0	5087	— 5	+ 4	5208	7.3	5214	— 6	+ 3
+ 9	5424	13.0	5447	— 23	— 13	5570	6.2	5574	— 4	+ 6
+ 10	5801	13.3	5807	— 6	+ 4	5924	7.6	5934	— 10	0
+ 11	6170	13.6	6167	+ 3	+ 13	6313	7.8	6294	+ 19	+ 29
+ 12	6497	13.1	6527	— 30	— 21	6640	6.2	6654	— 14	— 5
+ 13	6892	13.1	6887	+ 5	+ 12	6998	7.5	7014	— 16	— 9
+ 14	7230	13.7	7247	— 17	— 12	[7374]	[7.2]	7374		
		13.03			± 8		6.80			± 7

und schwankte unregelmässig um einen mittleren Betrag von 361.68 Tagen. PRAGER's Katalog für 1933 gibt den Periodenwert $361^{\text{d}}.1$, und das aus sämtlichen von mir seit d.J. 1906 in den *Astr. Nachr.* mitgeteilten Epochen der Minima und Maxima abgeleitete allgemeine Mittel ist 360^{d} .

Die extremen Werte des Lichtwechsels sind:

$$\begin{aligned} \text{Minimum: } v &= 13^{\text{m}}.03 \pm 0^{\text{m}}.081 \\ \text{Maximum: } v &= 6.80 \pm 0.124 \end{aligned} \quad \left. \vphantom{\begin{aligned} \text{Minimum: } v &= 13^{\text{m}}.03 \pm 0^{\text{m}}.081 \\ \text{Maximum: } v &= 6.80 \pm 0.124 \end{aligned}} \right\} \text{ (m.F.).}$$

Die Amplitude beträgt somit $6^{\text{m}}.23$. Sowohl beim Minimum wie beim Maximum scheinen die Abweichungen vom Mittelwert regellos aufzutreten.

Die Ableitung einer mittleren Kurve war diesmal mit grossen Schwierigkeiten verknüpft. In meinen früheren provisorischen Berichten nannte ich die Kurve oft schlängelnd, und tatsächlich treten sekundäre Wellen sowohl beim Auf- wie auch beim Abstieg auf; sie sind aber beim Aufstieg so selten (s. die Maxima 0546, 4487, 6640) und mit einer Ausnahme (0546) so wenig deutlich ausgeprägt, dass ich die Realität dieser Unregelmässigkeiten bezweifeln möchte. Ganz anders ist die Sachlage beim Abstieg.

TABELLE IV.

E	A. Wendepunkte				B. Ungestörte Maxima			
	B	v	R	B-R	B	v	R	B-R
- 13	²⁴¹ 7758	^m 9.4	7744	+ 14	—	—	—	—
- 12	8081	9.5	8104	- 23	²⁴¹ 8004	^m 6.7	8017	- 13
- 11	8456	9.1	8464	- 8	8373	5.1	8377	- 4
- 10	8816	9.7	8824	- 8	8723	6.2	8737	- 14
- 9	9194	9.4	9184	+ 10	9091	5.4	9097	- 6
- 8	9543	9.7	9544	- 1	9455	5.3	9457	- 2
- 7	9900	9.6	9904	- 4	9828	6.7	9817	+ 11
- 6	²⁴² 0277	9.7	0264	+ 13	²⁴² 0195	6.6	0177	+ 18
- 5	0642	9.4	0624	+ 18	0552	5.0	0537	+ 15
- 4	0980	9.9	0984	- 4	0904	6.7	0897	+ 7
- 1	2078	9.7	2064	+ 14	1992	5.2	1977	+ 15
+ 2	3136	9.7	3144	- 8	3055	7.0	3057	- 2
+ 3	3497	8.9	3504	- 7	3415	5.8	3417	- 2
+ 4	3849	8.5	3864	- 15	3778	5.6	3777	+ 1
+ 5	4234	10.3	4224	+ 10	4125	5.8	4137	- 12
+ 6	4582	9.7	4584	- 2	4488	6.1	4497	- 9
		9.51				5.95		

In 7 Fällen verläuft die Kurve glatt, in 20 Fällen tritt aber eine Verzögerung oder ein Stillstand auf. In 16 Fällen war es möglich, den Wendepunkt mehr oder weniger genau zu bestimmen. Die Epochen dieser Wendepunkte, nebst einer Vergleichung mit den Elementen R :

$$2422424^d + 360^d E,$$

findet man in der Tabelle IV A. Die Helligkeit in dieser Phase des Lichtwechsels ist

$$9^m.51 \pm 0^m.104 \text{ (m.F.)}.$$

Bei der Bildung der Kurve verfuhr ich übrigens wieder so wie es früher (Proc. 34, 220) beschrieben wurde. Für die Ableitung der Wendepunkts-Teilkurve wurden selbstverständlich auch die glatten Abstiege, bei deren fast linearem Verlauf der Wendepunkt willkürlich angenommen werden kann, berücksichtigt. Die drei Teilkurven schliessen sich genau an einander an (Fig. 2) und liefern zusammen die mittlere Kurve B (Tabelle V).

TABELLE V. Die mittlere Kurve.

Phase	v	Phase	v	Phase	v	Phase	v	Phase	v
— 100 ^d	10.69 ^m	— 30 ^d	12.80 ^m	+ 40 ^d	12.42 ^m	+ 110 ^d	7.16 ^m	+ 190 ^d	8.63 ^m
— 90	11.06	— 20	12.92	+ 50	12.02	+ 120	6.86	+ 200	9.00
— 80	11.42	— 10	13.00	+ 60	11.44	+ 130	6.80	+ 210	9.30
— 70	11.77	0	13.03	+ 70	10.59	+ 140	6.92	+ 220	9.56
— 60	12.09	+ 10	12.98	+ 80	9.65	+ 150	7.17	+ 230	9.80
— 50	12.37	+ 20	12.87	+ 90	8.54	+ 160	7.50	+ 240	10.03
— 40	12.61	+ 30	12.69	+ 100	7.73	+ 170	7.87	+ 250	10.32
						+ 180	8.25	+ 260	10.69

Eine „ungestörte“ Kurve konnte diesmal nur in 15 Fällen (s. die Fig. 1) zwanglos gezogen werden. Die Tabelle IV B gibt die Vergleichung mit den einfachen Elementen R :

$$2422337^d + 360^d E.$$

Die maximale Helligkeit wird

$$6^m.38 \pm 0^m.164 \text{ (m.F.)}.$$

Bei der Bildung der mittleren ungestörten Kurve müssen selbstverständlich auch die normalen Maxima mitstimmen. Auch diese als Mittel aus 15 ungestörten und 12 beobachteten Maxima konstruierte Teilkurve A schliesst sich den beiden anderen vollständig an. Für die Schiefe findet man:

$$\frac{M-m}{P} = 0.361.$$

Die Differenzkurve $C = A - B$ zeigt diesmal ein langgedehntes stationäres Minimum, zu 0^m.50 (Dauer 70^d), das den Stern von 37 % seines

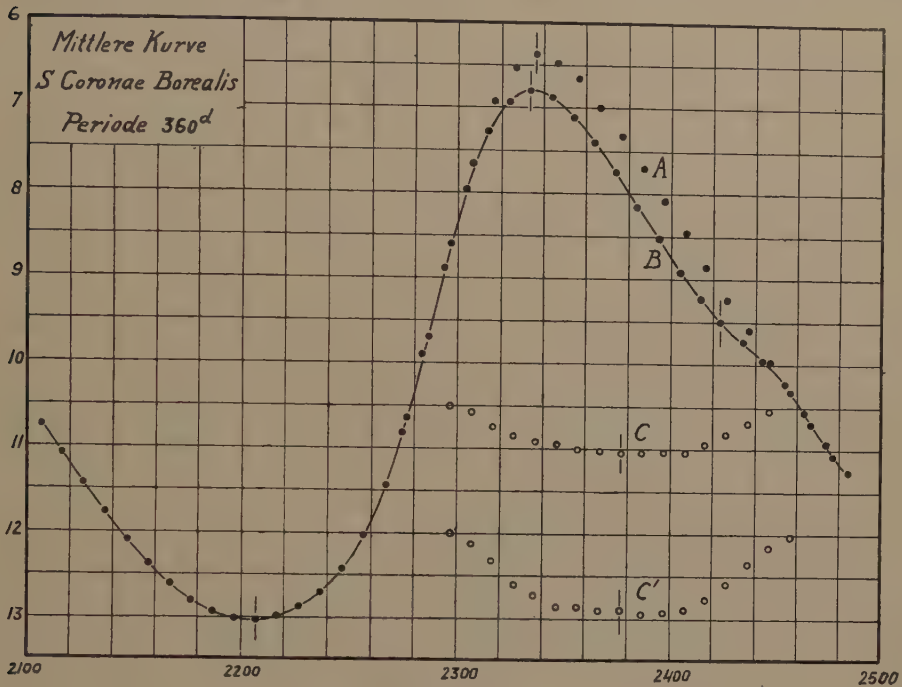


Fig. 2

Lichtes beraubt; die Mitte der Verfinsterung fällt auf 2422378.

Man kann aber auch hier, wie bei *R Leonis min.* (Proc. 35, 937), die Auffassung verteidigen, dass *S Cor. bor.* nur in gewissen Fällen eine Verdunkelung erleidet. Werden diese 15 Verdunkelungskurven einzeln bestimmt, und dann zu einer mittleren Kurve vereinigt, so entsteht die Kurve C' (Mitte der Verfinsterung 2377, also 43^d nach dem beobachteten Maximum; Dauer der stationären Phase 70^d). Im Minimum, zu 0^m.90, erleidet das Licht des Sterns einen Verlust von 56 %. Die zweite Auffassung kommt mir die wahrscheinlichere vor.

Utrecht, Dezember 1933.

Chemistry. — *On Complex Salts with α - α' -Dipyridyl: Complex Salts of bivalent Nickel.* By F. M. JAEGER and J. A. VAN DIJK.

(Communicated at the meeting of December 16, 1933.)

§ 1. In the course of a study of the complex α - α' -dipyridylsalts of the metals *nickel*, *iron*, *cobaltum* and *rhodium*, we observed that most of these metals were able to yield different series of such complex salts, their occurrence being dependent on the special circumstances during the preparation. In this paper we only wish to communicate some results obtained in the study of the complex salts of bivalent *nickel*.

The *tridipyridyl* salt of nickel-chloride was already described by BLAU¹⁾; this and other salts were studied more in detail by MORGAN and BURSTALL²⁾, who first succeeded in resolving the complex cation into its optically-active components. More recently, PFEIFFER and TAPPERMANN³⁾ studied the complex salts of *nickel* with α - α' -dipyridyl and *o*-phenanthroline; their results, although compatible with ours in general lines, deviate, however, from our experiences in some details which, on the other hand bring a happy completion of the facts hitherto stated.

The base used in these experiments was prepared in appreciable quantities after the method of HEIN and RETTER⁴⁾, by the interaction of anhydrous ferric chloride on pyridine in sealed tubes at 300° C. It crystallizes from ethylacetate in big, lustrous monoclinic crystals, with: $a:b:c=0.8915:1:1.8701$ and $\beta=85^{\circ} 16'$, which are limited by the forms: $\{101\}$, $\{\bar{1}01\}$ and $\{011\}$. Their meltingpoint is 71° C. The compound is volatile; its vapours have an agreeable, somewhat sweet odour.

The crystalforms of α - α' -dipyridyl are reproduced in Fig. 1¹ and 1³ for the crystals obtained from ether, in Fig. 1² and 1⁴ for those deposited from ethylacetate.

Forms observed: $s=\{\bar{1}01\}$, very lustrous, usually predominant; $r=\{101\}$, smaller than s , yielding good reflections; $q=\{011\}$, giving very sharp images and usually strongly developed.

¹⁾ F. BLAU, Monatshefte f. Chemie, **19**, (1898), 647.

²⁾ G. T. MORGAN and F. H. BURSTALL, Journ. Chem. Soc. London, (1931). II, 2213.

³⁾ P. PFEIFFER and F. TAPPERMANN, Zeits. f. anorg. Chem. **215**, (1933), 273.

⁴⁾ F. HEIN and W. RETTER, Ber. d. d. chem. Ges., **61**, (1928), 1790; conf. also: J. P. WIBAUT, Rec. Trav. Chim. Pays-Bas, **47**, (1928), 761.

Angular Values:	Observed:	Calculated:
$q : q = (011) : (0\bar{1}\bar{1}) = ^\star$	$56^\circ 26'$	—
$r : s = (101) : (10\bar{1}) = ^\star$	50 53	—
$q : s = (011) : (\bar{1}01) = ^\star$	79 59	—
$q : r = (011) : (101) =$	76 39	$76^\circ 37'$

No distinct cleavability was observed.

Optically biaxial; the plane of the optical axes is $\{010\}$. On $\{\bar{1}01\}$ one of the hyperbolic branches is observed; the very strong dispersion is: $\rho < \nu$.

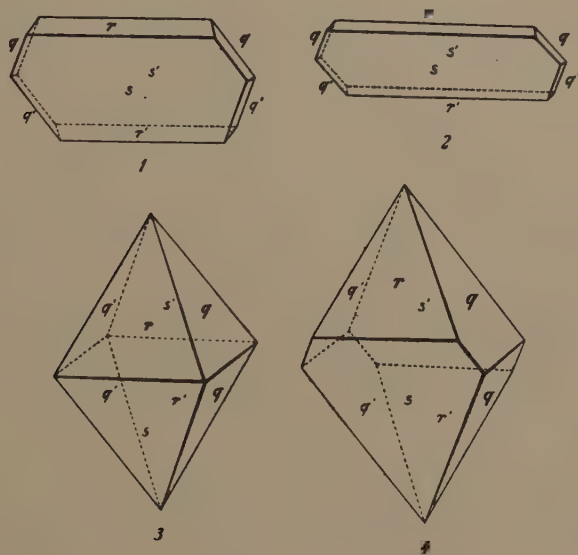
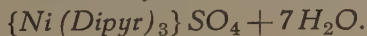


Fig. 1. Crystalforms of α - α' -Dipyridyl.

If a solution of 2.5 Gr *nickelsulphate* ($+7H_2O$) is mixed with an alcoholic solution of 4.7 Gr *dipyridyl*, the solution turns to a deep red. On evaporation on the waterbath, a red salt is obtained in beautiful monoclinic crystals, which have the composition:



Analysis: Ni: 7.80 %, calc. 7.83 %; SO_4 : 12.85 %, calc. 12.82 %; N: 11.17 %, calc. 11.22 %; H_2O : 16.8—17.0 %, calc. 16.81 %.

Occasionally some blue needles appeared intermixed with the red crystals. A more detailed examination taught us, that they are formed from the red salt, if an excess of *nickelsulphate* is present. If a solution of 2 equivalents of $NiSO_4 + 7H_2O$ be added to a solution of the red salt the colour of the solution, on heating on the waterbath, turns to a deep blue, and, on slow evaporation, only the blue salt is deposited from it in needles which have the aspect of *coppersulphate*. The same salt is also produced,

if a solution of nickelsulphate is mixed with an alcoholic solution of 1 equivalent of dipyridyl: the solution turns red during a very short interval of time, then rapidly gets blue and on evaporation the same blue needles as mentioned are deposited on cooling. They are triclinic, only sparingly soluble in cold, better in hot water; they have the composition: $\left\{ \text{Ni} \begin{smallmatrix} (\text{Dipyr}) \\ (\text{H}_2\text{O})_2 \end{smallmatrix} \right\} \text{SO}_4 + 4 \text{H}_2\text{O}$. At 100°C . only $4 \text{H}_2\text{O}$ are expelled, but not the two water-molecules of the complex ion.

Analysis: Ni: 13.96 %, calc. 14.01 %; SO_4 : 22.5 %, calc. 22.93 %; N: 6.67 %, calc. 6.68 %; H_2O : 16.85 %, calc. 17.2 %.

If the crystallized, finely pulverized nickelsulphate ($+ 7 \text{H}_2\text{O}$) is added to a concentrated solution of the red tridipyridylsalt, (2 equiv. of the sulphate $+ 1$ equiv. of the red salt) and the mixture, under continually stirring, be heated on the waterbath, the solution turns to a deep indigo-blue colour; on cooling, an aggregate of long, pale blue, hair-like needles is deposited, which have the same composition as the blue needles previously mentioned. They evidently represent a second modification of the blue salt; after dissolving them in water, they yield a pale blue solution, from which the ordinary triclinic needles are once more deposited.

§ 2. *Tridipyridylnickelsulphate* ($+ 7 \text{H}_2\text{O}$) crystallizes in deep pink, monoclinic crystals (Fig. 2). They are very lustrous, hard and well developed; in most cases they have the aspect of thick plates (Fig. 2A), sometimes of rectangular flattened crystals. (Fig. 2B).

Monoclinic-prismatic.

$$a:b:c = 1.5342:1:0.9134; \beta = 82^\circ 19\frac{1}{2}'$$

Forms observed: $a = \{100\}$, either small or predominant, always yielding very sharp reflections; $m = \{110\}$, very lustrous; $r = \{\bar{1}01\}$, often strongly predominant and always broader than $s = \{101\}$; both forms give very good reflections.

Moreover, $q = \{011\}$, small and yielding dull images.

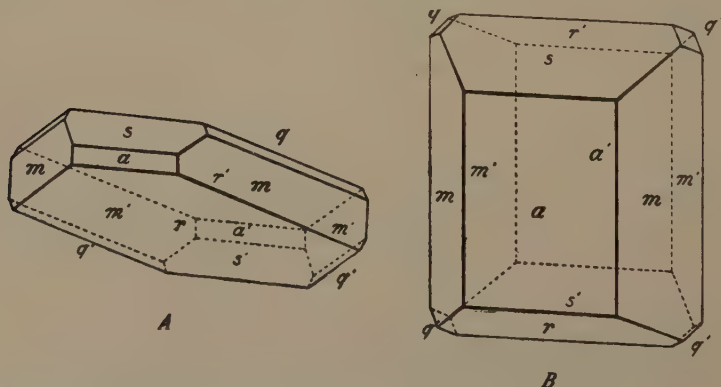


Fig. 2. Crystalform of *Tridipyridyl-Nickelsulphate* ($+ 7 \text{H}_2\text{O}$).

<i>Angular Values:</i>	<i>Observed:</i>	<i>Calculated:</i>
$a : m = (100) : (110) = *$	56° 40'	—
$r : s = (\bar{1}01) : (101) = *$	61 19	—
$a : r = (100) : (10\bar{1}) = *$	65 1	—
$m : q = (110) : (011) =$	52 6	52° 3½'
$r : q = (\bar{1}01) : (011) =$	51 19	51 22½'
$m : q = (110) : (0\bar{1}1) =$	59 32	59 35
$m : s = (\bar{1}10) : (101) =$	71 8	71 0
$m : r = (110) : (10\bar{1}) =$	76 35	76 35
$a : s = (100) : (101) =$	53 40	53 40
$m : m = (110) : (\bar{1}10) =$	66 40	66 40
$s : q = (\bar{1}0\bar{1}) : (01\bar{1}) =$	49 20	49 25

No distinct cleavability was observed.

The optical axial plane is $\{010\}$; inclined dispersion. On $\{100\}$ the crystals are strongly dichroitic: for vibrations parallel to the c -axis pale-red, for such parallel to the b -axis blood-red. One of the optical axes emerges on $\{100\}$ almost perpendicularly to this plane.

The salt is a derivative of a moderately strong complex cation. On heating with strong nitric acid or aqua regia, it is decomposed; but as long as dipyridyl is present in the solution, the complex ion afterwards is regenerated and the solution, on evaporation, again turns red. For the purpose of analysis the salt was destructed by carefully melting it with soda and sodiumnitrate. Ammonia yields no precipitate in the solution of the salt, not even at boiling-temperature, sodiumhydroxide at room-temperature gives a slight precipitate; on boiling, dipyridyl is set free, but the greenish solution later-on again gets colourless. Strong nitric acid (1.30) does not attack the substance at room-temperature; on boiling, the liquor gets blue and, on cooling, violet. Strong hydrochloric acid behaves in an analogous way, the solution, on boiling, assuming a green colour, which, on cooling, turns to blue or bluish-violet. Aqua regia renders the solution colourless; later-on it gets green. A solution of bromine in water yields a yellow or orange precipitate, on heating, the solution turns a pale-pink and a reddish precipitate is formed.

On heating with a strong solution of yellow ammoniumsulphide, a black precipitate of NiS is slowly formed, but the decomposition is incomplete and can only be performed by repeatedly heating of the substance with an excess of fresh ammoniumsulphide-solution.

§ 3. *Monodipyridyl-diaquo-nickelsulphate* (+ 4 H_2O) crystallizes from its pale-blue solutions in beautiful, blue needles. The crystals are triclinic, long prisms with a flattening parallel to $\{010\}$; this form shows a very fine vertical striation. Also $\{100\}$ has such a striation parallel to the c -axis; doubtlessly the crystals possess a polysynthetic lamellar structure parallel to $\{100\}$ and $\{010\}$. In the zone of the c -axis the angular values, because of the occurrence of vicinal faces, often oscillate within wider limits.

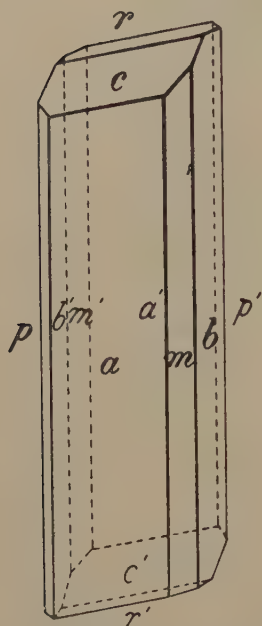


Fig. 3. Crystalform of *Monodipyridyl-diaquo-Nickelsulphate* (+4 H_2O).

Triclinic-pinacoïdal.

$$a : b : c = 1.8786 : 1 : 1.2179.$$

$$A = 75^\circ 58' ; \quad \alpha = 75^\circ 58'$$

$$B = 127 \quad 54 ; \quad \beta = 127 \quad 54$$

$$C = 58 \quad 2 ; \quad \gamma = 94 \quad 58$$

Forms observed: $a = \{100\}$, smooth, well reflecting, often vertically striated; $b = \{010\}$ broader than a , always finely striated, yielding coloured or multiple, somewhat dull reflections, $c = \{001\}$, well developed, very lustrous and, like $r = \{101\}$, giving sharp reflections; $m = \{110\}$, narrow, sometimes equally broad as a ; $p = \{1\bar{1}0\}$, very narrow, often absent. The habitus is long-prismatic in the direction of the c -axis. (Fig. 3.)

Angular Values:

Observed: Calculated:

$a : b = (100) : (010) =^*$	$94^\circ 58'$	—
$b : c = (0\bar{1}0) : (001) =^*$	$104 \quad 2$	—
$c : a = (001) : (100) =^*$	$52 \quad 6$	—
$c : r = (001) : (\bar{1}01) =^*$	$39 \quad 8$	—
$m : a = (110) : (100) =^*$	$60 \quad 19$	—
$m : b = (110) : (010) =$	$34 \quad 39$	$34^\circ 39'$
$b : p = (0\bar{1}0) : (1\bar{1}0) =$	$31 \quad 37$	$31 \quad 44$
$p : a = (1\bar{1}0) : (100) =$	$53 \quad 25$	$53 \quad 18$
$r : a = (\bar{1}01) : (\bar{1}00) =$	$88 \quad 46$	$88 \quad 46$
$b : r = (010) : (\bar{1}01) =$	$76 \quad 39$	$76 \quad 8$

No distinct cleavability was observed.

The optical extinction on all faces of the vertical zone is oblique to the

boundaries of the different planes: on {010} it makes an angle of about 42° with respect to the *c*-axis.

The crystals are dichroïtic: on {010} pale-blue and dark-blue; on {100} bluish-white and pale-blue. On {010} one of the optical axes emerges at the border of the image; one axis is almost perpendicular to {110}, and a conical refraction is observed. The axial plane is inclined at about 42° with respect to the *c*-axis. The dispersion is appreciable.

§ 4. Tentatives were also made with the purpose of preparing a salt with 2 molecules of dipyridyl in the complex cation. Two equivalents of the red salt in solution were, therefore, mixed with a solution of 1 equivalent of $\text{NiSO}_4 + 7 \text{H}_2\text{O}$. A reddish-violet solution thus was obtained, from which, however, on slow evaporation only crystals of the red and the blue salts besides each other were deposited. Also on mixing a solution of the blue salt with an alcoholic solution of 1 equivalent of dipyridyl, only a mixture of the blue salt and the dipyridyl in excess could be obtained.

Evidently, therefore, it is impossible in aqueous solutions to obtain a salt of the type: $\{\text{Ni}(\text{Dip})_2\} \text{X}_2$. This experience is in accordance with that of PFEIFFER and TAPPERMANN¹⁾, who also were unable to obtain a salt of the composition: $\{\text{Ni}(\text{Dipyr})_2\} \text{X}_2$ from aqueous solutions. However, they prepared a green salt: $\{\text{Ni}(\text{Dipyr})_2\} \text{Cl}_2$ by carefully heating the previously dehydrated tridipyridyl-salt: one molecule of the base then is expelled and the green salt of the said composition is formed. This, however, proved to be unstable in aqueous solution, the red tridipyridyl-salt then being regenerated.

A similar reaction is produced, when the blue solution of the salt: $\left\{ \text{Ni} \begin{smallmatrix} (\text{Dipyr}) \\ (\text{H}_2\text{O})_2 \end{smallmatrix} \right\} \text{SO}_4 + 4 \text{H}_2\text{O}$ at room-temperature is treated with the right quantity of bariumhydroxide: a greenish, colloidal precipitate is produced and the colour of the solution once more gets red. Evidently the reaction: $3 \left\{ \text{Ni} \begin{smallmatrix} (\text{Dipyr}) \\ (\text{H}_2\text{O})_2 \end{smallmatrix} \right\} \text{SO}_4 + 4 \text{H}_2\text{O} + 3 \text{Ba}(\text{OH})_2 = \{\text{Ni}(\text{Dipyr})_3\}(\text{OH})_2 + 2 \text{Ni}(\text{OH})_2 + 3 \text{BaSO}_4 + 18 \text{H}_2\text{O}$ takes place, the precipitate formed being a mixture of bariumsulphate and nickelhydroxide.

*Groningen, Laboratory for Inorganic and Physical Chemistry
of the University.*

¹⁾ loco cit., p. 277.

Physics. — *Détermination des Intensités Relatives des Composantes du Multiplet $a^3F-y^3F^0$ de FeI .* Par J. PIÉRAND. (Communication de l'Institut de Physique de l'Université d'Utrecht.) (Communicated by Prof. L. S. ORNSTEIN.)

(Communicated at the meeting of December 16, 1933.)

A. Introduction.

Dans un article intitulé: "On the intensities of STELLAR Absorption-lines¹⁾", O. STRUVE et W. W. MORGAN ont trouvé, dans les étoiles, des différences d'intensités relatives dans les doublets et quadruplets de OII ainsi que dans les multiplets de FeI , $FeII$ et $TiII$. Les intensités relatives des composantes ne sont pas les mêmes, bien que les potentiels d'excitation soient pratiquement identiques. Des différences similaires pour les multiplets de FeI furent établies par W. W. MORGAN dans plusieurs étoiles de classe A.

Le multiplet $a^3F-y^3F^0$ de FeI est un de ceux où les différences sont les plus notables. Le tableau suivant montre le degré d'intensité pour les lignes de ce multiplet dans différentes étoiles.

TABLEAU 1²⁾.

Raies	ΔJ	I. Lab.	Sol.	λ ptc.	σ^1 cmi.	22 Boo	ξ Ser.	e^2 Vir.	2 Mon.	Theor.
3969.263	4—3	20 III	10	—	—	—	—	—	—	81
4005.250	3—2	25 II	7	4	4	5—6	7	6	5	80
4045.822	4—4	60 R. II	30	4	5	9	7—9	7	8	1215
4063.604	3—3	45 II	20	3—4	3	3	4—5	5	4	847
4071.748	2—2	40 II	15	3—4	3	2	2—3	3	2	640
4132.064	3—4	25 II	10	1	2	2	2	3	2—3	81
4143.874	2—3	30 I	15	3—4	4	3—4	4—5	4	4	80

Nous avons repris la détermination expérimentale des intensités des composantes de ce multiplet en émission, en essayant de faire varier les conditions physiques. Comme la mesure des intensités des raies spectrales

¹⁾ O. STRUVE et W. W. MORGAN. Proceedings of the national Academy of Sciences Vol. 18, N^o. 9, pp. 590—594. September 1932.

²⁾ Tableau tiré du même article. que (1).

est presque toujours rapportée à des échelles arbitraires, celles-ci variant avec l'observateur, nous avons voulu apporter plus de précision en nous servant de plaques standardisées soigneusement et en faisant un choix convenable d'étalons photométriques.

B. Dispositif Expérimental.

Le problème de la détermination des intensités nécessite la construction d'une série d'écrans ne laissant passer qu'un pourcentage bien connu de lumière, nous avons construit cette série d'écrans en nous basant sur la méthode décrite par L. S. ORNSTEIN, MOLL et BURGER¹⁾. Les différents pourcentages de transparence de notre série d'échelons photométriques sont résumés dans le tableau suivant.

TABLEAU No. 2 (domaine des longueurs d'onde) 3900—4200 Å.

Premier échelon laisse passer	100 ⁰ / ₀	de lumière
Deuxième échelon laisse passer	65 ⁰ / ₀	" "
Quatrième échelon laisse passer	29 ⁰ / ₀	" "
Cinquième échelon laisse passer	18 ⁰ / ₀	" "
Sixième échelon laisse passer	11.5 ⁰ / ₀	" "
Septième échelon laisse passer	100 ⁰ / ₀	" "

Le dispositif optique est celui décrit dans le livre "Objektive Spektral-photometrie ²⁾ car nous avons employé un spectrograph à réseau (ROWLAND stigmatique). Nous sommes parvenus à éliminer la réabsorption en diminuant la concentration du fer dans l'arc. Nous avons utilisé des électrodes d'argent avec 1 % de fer et nous avons abaissé le courant dans l'arc jusqu'à 1 Ampère, 8 et 1 Ampère, 2. La faible concentration en atomes de fer nous a malheureusement obligé d'augmenter le temps de pose (6 heures), pour obtenir, d'une façon suffisante, les raies les plus faibles du multiplet. La réabsorption nous a empêché d'augmenter d'une façon conséquente l'intensité du courant dans l'arc afin de constater des variations d'intensité en fonction du courant.

C. Résultats.

Pour déterminer l'intensité relative de chacune des raies, nous avons également employé la méthode des mesures d'intensité sans source de lumière auxiliaire par L. S. ORNSTEIN, MOLL et BURGER³⁾.

¹⁾ L. S. ORNSTEIN, W. S. H. MOLL und H. C. BURGER. Objektive Spektralphotometrie (Vieweg & Sohn, Braunschweig. 1932).

²⁾ Loc. cit.

³⁾ Loc. cit.

Le tableau n^o. 3 donne les valeurs des intensités relatives des composantes du multiplet déduites des courbes de noircissement de chacune des raies du multiplet. La raie $\lambda = 4045 \text{ \AA}$ étant la plus intense, nous lui avons donné la valeur 100.

TABLEAU No. 3 (arc de 1 Ampère, 8).

Raies	1. relat. obs.	Int. théoriques	ΔJ
$\lambda = 3969 \text{ \AA}$	25	6.66	4-3
$\lambda = 4005 \text{ \AA}$	20	6.66	3-2
$\lambda = 4045 \text{ \AA}$	100	100	4-4
$\lambda = 4063 \text{ \AA}$	70	70	3-3
$\lambda = 4071 \text{ \AA}$	56	53.33	2-2
$\lambda = 4132 \text{ \AA}$	26	6.66	3-4
$\lambda = 4143 \text{ \AA}$	21	6.66	2-3

I. Application de la règle de somme.

Nous avons essayé d'appliquer la règle de somme à ce multiplet afin de vérifier si nos valeurs avaient le poids désiré. Nous avons rangé les valeurs des intensités dans le tableau suivant.

TABLEAU No. 4.

J	4	3	2	Tot.
4	100 (100)	25 (6.6)		125
3	26 (6.6)	70 (70)	20 (6.6)	116
2		21 (6.6)	56 (53)	77
Tot.	126	116	76	

Les valeurs mises, entre parenthèses, sont les intensités théoriques trouvées par application des formules de SOMMERFELD ; les autres nombres sont les intensités relatives que nous avons obtenues. Les totaux des intensités, en vertical et en horizontal, ne sont pas bien dans le rapport $2j + 1$ c'est-à-dire comme 9:7:5, mais bien comme 8.3:7.6:5. Comme les trois raies les plus intenses ont des intensités relatives conformes aux

valeurs théoriques déduites des formules de SOMMERFELD¹⁾, ce désaccord provient certainement des raies dont les intensités théoriques sont égales à 6.6, qui ont ici une intensité relative observée trop forte. Cela peut provenir d'erreurs d'ordre expérimental, (réabsorption) ou causé par le fait que la règle de somme étendue devrait être appliquée.

E. Variations d'Intensité en Fonction du Courant.

Notre but était de rechercher les variations d'intensité, au sein d'un même multiplet, en modifiant certaines conditions physiques telles que courant, pression, etc. . . De nombreuses difficultés expérimentales ne nous ont pas permis de faire pour le moment des mesures quantitatives de ces variations. Nous n'avons pu opérer que de faibles variations de courant. Les variations d'intensités relatives, que nous avons enregistrées pour un arc de 1 Ampère, 8 et 1 Ampère, 2 sont relativement faibles et de l'ordre de 6 à 7 %. Ce pourcentage ne nous permet pas de conclusion d'ordre quantitatif, car il peut provenir d'erreurs expérimentales. Pour d'aussi faibles variations de courant, la température, au sein de l'arc n'augmente guère; par conséquent, il ne peut théoriquement exister de variations d'intensité appréciables. Il est certain que dans les étoiles, les variations de température et de pression doivent être plus considérables même pour les étoiles d'une même classe.

En terminant, je tiens à exprimer mes remerciements à Monsieur le Prof. Doct. ORNSTEIN pour sa cordiale hospitalité et pour l'aide précieuse qu'il n'a cessé de me prodiguer, durant mon séjour à l'Institut de Physique d'Utrecht.

Septembre 1933.

¹⁾ Atoms. Molecules et quanta. RUARK and UREY.

Physics. — *The lyotropic series and the spreading of proteins.* By
EVERT GORTER, M.D. (Leiden). (Communicated by Prof. J. VAN
DER HOEVE).

(Communicated at the meeting of December 16, 1933.)

I have studied the effect of different ions on the spreading of proteins. As I have shown previously¹⁾ the effect of uni- bi- and trivalent ions has a very different effect, in so far as a much smaller amount of the ions of higher valency is sufficient to produce the same effect.

Now, I have been able to show that on the acid side (at pH 3) of the iso-electric point and using again pure ovalbumin as a protein, the effect of different univalent ions is different according to their place in the lyotropic series. The effect on the spreading of an univalent anion is higher the more to the right it is placed in the series (fig. 1) :

Cl^- , Br^- , I^- , CNS^- .

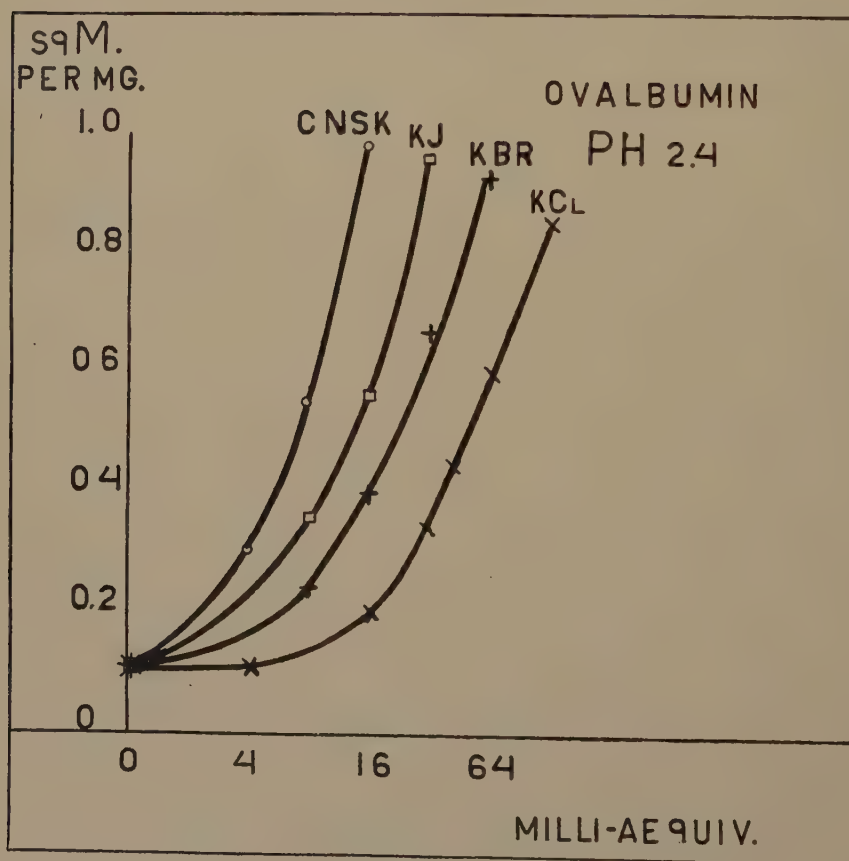


Fig. 1.

¹⁾ Proc. Kon. Ak. van. Wet. XXXV N^o. 6, 1932.

The same observation can be made with regard to the effect of univalent kations on the spreading, on the alkaline side of the iso-electric point (pH 6) of a protein. Now it is easier to use pepsin, having an iso-electric point at pH 2.85.

Here again the spreading shows a minimum. The influence of a kation is stronger the further to the right it is placed in the series (fig. 2):

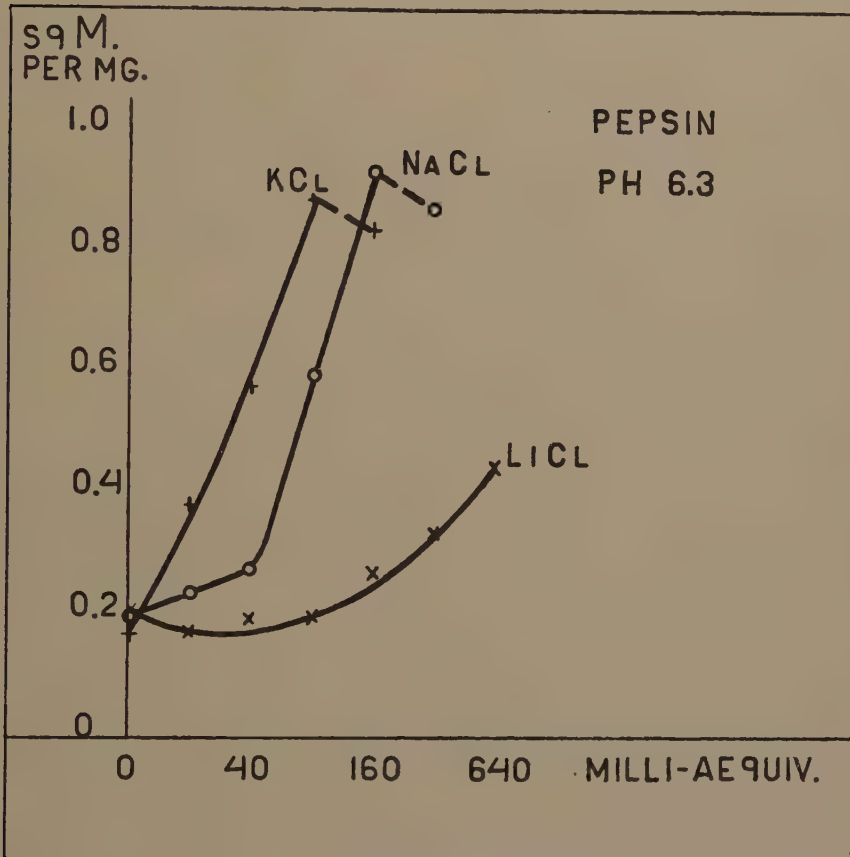
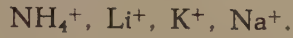


Fig. 2.

I have not succeeded to demonstrate a difference of the influence of different bi-valent kations.

Mg^{++} , Ca^{++} , Sr^{++} , Ba^{++} , have the same influence on the spreading in an amount of some milli-equivalents only, but I was unable to find any difference between the members of this series (fig. 3).

The solution of pH 3 was a 0.001 molar hydrochloric acid in pure distilled water, the solution pH 6 was a mixture of 0.001 molar hydro-

chloric acid and 0.001 molar sodium hydroxyde. The use of strong buffer solutions is impossible because of the effect of ions on the spreading.

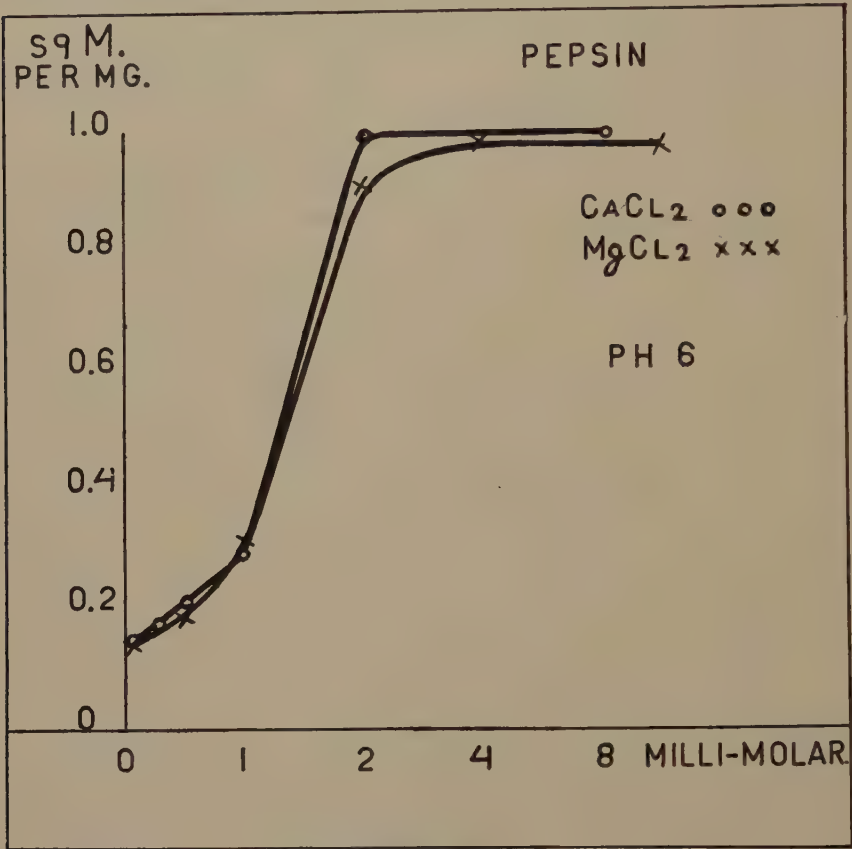


Fig. 3.

Bivalent ions have a strong influence and cannot be made use of for this reason even in high dilutions.

Geology. — *On the occurrence of Interglacial (Risz-Würm) Peat in Holland.* By G. G. LOUMAN. (Communicated by Prof. H. A. BROUWER).

(Communicated at the meeting of December 16, 1933.)

Hitherto nothing was known about the forest-development in the last interglacial period (Eemien) in Holland.

A pollenanalytic investigation of peat- and clay-samples from Baarn, the Wieringermeer and Amersfoort has enabled me to state in the first place their interglacial age, in the second place to give an idea of the

forest- and climate-development at the time of the clay-sedimentation and the peat-forming.



Map showing the coastline of the EEM SEA in HOLLAND
D.J.F. STEENHUIS "DE INGENIEUR" 1933 N° 22.

It will be apparent from this investigation that a complete alteration in the character of the vegetation has taken place after the regression of the warm Eem-sea. The temperature gradually decreased and the climate grew cooler in consequence of a new approaching of glaciation.

I. Borings of the Geological Survey in the vicinity of Baarn (36 K.M. S.E. of Amsterdam) and Wieringermeer (60 K.M. N. of Amsterdam) proved that above Eem-strata plantbearing beds were lying.

The profile of three borings produced the following strata:

BAARN:

Boring 4	Boring 1	Boring 16
N. A. P. 0.00— 2.70 clay	N. A. P. + 0.20—0.00 peat	N. A. P. 0.20—0.90 clay
2.70— 6.30 peat	0.00—5.00 sand	0.90—3.30 peat
6.30— 6.80 sand	III 5.00—7.70 peat	3.30—4.90 sand
I 6.80— 9.70 peat	IV 7.70—8.55 clay	V 4.90—8.65 sandy- peat
II 9.70—11.20 clay	8.55— sand	8.65—9.45 sand
11.20— Eem-strata		

WIERINGERMEER:

Boring R

0.00—3.60 M. (below surface) greyish clay

3.60—3.80 M. postglacial peat

3.80—6.35 M. sand

VI 6.35—6.65 M. dark humous clay-mud

VII 6.65—8.00 M. sandy clay, greyish

I received samples from the strata I, II, III, etc.

Pollenanalysis of these samples gave the following spectra:

No.	Sa	Be	Pin	Pic	Al	Qu	Til	Ul	EMW	Ab	Car	Fag	Cor	Sph	Eric
I	0.7	31.7	61.3	0.7	3.3	0.7	—	—	0.7	0.7	—	—	4	88	43
Ia	0.7	20.7	60	8	6	2.7	—	—	2.7	0.7	1.3	—	2	46	55
II	—	—	18.3	50.8	7.5	5.8	—	—	5.8	10	7.5	—	2	5	1
III	—	32.5	42.5	13	1	0.5	—	—	0.5	10	—	—	—	27	53
IV	—	3.3	14	22	28.7	5.3	0.7	—	6	12	14	—	8	13	6
V	0.7	14	56.7	21.3	4.7	2	—	—	2	1.3	—	—	2	130	31
VI	—	—	10	78	5	2	—	—	2	—	5	—	4	1	2
VII	—	6.8	6.8	10.3	46.7	4.8	3.4	0.7	9	2.7	17.6	—	26.3	—	1

The flora of these bogs with *Picea*, *Carpinus* and *Abies* in such quantities, and the lack of *Fagus*, characterize them as unquestionably interglacial. The pollendiagram furthermore can indicate the development of the forest-vegetation during the period of formation of the strata and this gives an idea of the climatic circumstances at the time of the regression of the Eem-sea in Holland.

In the clay-layers IV and VII there is a rather high frequency of *Carpinus*-pollen, together with *Alnus*, *Abies*, *Quercus*, *Tilia*, *Corylus*; so the *thermophile* species of the mixed oak-forest are still represented. Zone II and VI are characterized by the fact that *Picea*-pollen here attains absolute dominance (50 and 78 %), the other deciduous trees are decreasing. Thus, a pronounced coniferous period reigned. The climate grew cooler. The impoverishment of the forest-growth increases in the following zone I with a maximum of *Pinus*-pollen (61 %). Also III and V are distinguished from the previous ones by the fact that here *Pinus silvestris* has been the dominant species; *Betula* has a rather high frequency of 32 %. A Conifer-forest of northern character now covered these surroundings.

So we may distinguish in the diagrams three periods:

- 1) Pinus + Betula-zone
- 2) Picea-zone
- 3) Carpinus + Alnus + Abies-zone.

The recent distribution of *Abies* in Central Europe learns that *Abies* requires a good climate; it indicates a mildness of the climate, with much moisture, consequently an atlantic climate.

The following period with Picea-maximum indicates already a climate with cold winters. There are different views regarding the understanding of the western limit of distribution of *Picea excelsa* in Europe. As may be seen from the scheme of MILTHERS and JESSEN, they connect a Picea-maximum with a continental climate. I suppose, however, that at the time of the Picea-forest in Holland the climate was more subboreal¹⁾.

Finally the forests consisted almost exclusively of *Betula* and *Pinus*. It is in this period that the peat-stratum was formed: remains of *Sphagnum*, *Aulacomnium*, *Hypnum*, *Polypodium*, *Osmunda regalis* and a large quantity of *Ericales*, indicating a heath-vegetation in the surroundings. The climate was sub-arctic.

Hitherto only little is known about peat in connection with Eem-strata. MILTHERS and JESSEN in: "Interglacial Fresh-water Deposits in Jutland and Northwest Germany" describe the profile of the cliff at Stensigmose near Sønderborg. The peat, however, is lying here *below* the marine Eem-deposits and belongs to the *first* part of the last interglacial period (zones d and e).

The last interglacial period as well as the penultimate interglacial period show a complete cycle from an arctic via a mild temperate to a subarctic climate. This is expressed by the character of the flora (indicated by MILTHERS and JESSEN: zone a, b) which passes through a first Conifer-period (warmer, continental, zone c—e) into a flora of deciduous trees (oceanic climate, temperature optimum, zone f, g) culminating in the mixed oak-forests (*Quercus*, *Ulmus*, *Tilia*) jointly with *Corylus* and *Alnus*, then a *Carpinus*-period (zone g) terminating with the second Conifer-period (zone h = Picea-dominance, continental; zone i = *Betula* + *Pinus* dominant).

In connection with the peat lying under the Eem-strata MILTHERS and JESSEN write:

"The transgression of the Eem sea over the fresh water beds in Stensigmose cliff must then have taken place in the time of the mixed oak forest, during the last interglacial period. It is impossible to determine,

¹⁾ In Holland there hardly could have existed such a pronounced continental climate as the Picea-maximum would make suppose, the Eem-sea still being present in more or less extent. Afterwards this sea regressed by far more inward than the present coastline of the north-sea. DUBOIS supposed a rise of the land after the Eem-sea to such an extent, that the Channel between England and France dried up, together with great parts of the southern north-sea.

Fig. 2

No.	Depth below surface	Nature of sample	Sa	Be	Pin	Pic	Al	Qu	Til	Ull	EMW	Ab	Car	Fag	Cor	Sph	Eric
VIII	8.90—9.60 M	Peat	1	1	98	—	—	—	—	—	—	—	—	—	—	5	35
IX	10.20—12.10 M	Humous Clay	13.3	33.3	22.5	10	18.3	2.5	—	—	2.5	—	0.8	—	5	74	62
X	13.40—15.10 M	"	—	14.7	44.7	27.3	8	1.3	—	—	1.3	1.3	2.7	—	3.2	42	72
XI	26.60—26.80 M	"	1.5	4.6	27.6	—	32.3	33.8	—	—	33.8	—	—	—	62	—	1
XII	8.40—11.40 M	Peat	—	11	88	—	—	1	—	—	—	—	—	—	—	5	16
XIII	12.65—13.80 M	"	1.7	15.4	28	17.1	11.4	9.7	—	1.1	10.8	10.9	4.6	—	23.3	41	34
XIV	26.70—27.60 M	Humous Clay	0.8	4	32	—	44.8	14.4	0.8	3.2	18.4	—	—	—	60.4	—	1
XV	9.00—9.80 M	Peat (Ferns)	2	22	72	—	—	4	—	—	4	—	—	—	—	—	—
XVI	12.80—14.20 M	Clay	—	4	31	37	10	3	—	1	4	9	6	—	3.8	32	28

by pollen statistics, when the upheaval of land which again shut off the Baltic from the Eem sea occurred, as *no bogs resting on deposits from that sea are known*".

In the underlying material, however, we have found deposits formed after the regression of the Eem-sea and lying upon Eem-strata.

The pollenanalysis which showed a close agreement with the zones *g*, *h* and *i* of JESSEN's scheme has enabled to conclude that these bogs have been formed in the *last stage of the last interglacial period (Second Conifer-period)*.

II. The investigation of peat-samples out of the vicinity of Amersfoort brought a completing link in the foregoing. Here, not only peat-layers overlying Eem-strata were found, but also peat-formations covered by Eem-strata and lying upon deposits of the Riss-glaciation. Consequently they have been formed before the Eem-sea transgressed over this country.

The layers between X and XI and between XIII and XIV are deposits of the Eem-sea.

In zone XI *Quercus* (33 %) and *Corylus* (62 %) predominate; in XIV also *Tilia* and *Ulmus* occur. From these data it appears that the mixed oak-forest was very well developed. *Alnus* is culminating in XIV (44 %), *Pinus* is still of some importance, *Carpinus*- and *Picea*-pollen were not yet present. These strata below the Eem-layers have been formed at the end of the *first Conifer-period*; the coniferous trees were decreasing and replaced by forest of deciduous trees. The culmination of the latter will be found at the time when the warm Eem-sea had its greatest extension in this country.

Afterwards, when the sea regressed, the mixed oak-forest was still present, which is demonstrated by the pollendiagrams of Baarn, Wieringermeer and those of Amersfoort (XIII: EMW = 10 %). Also *Abies* and *Carpinus* occur. Gradually, the temperature decreased and the winters grew colder (*Picea*-zone); the coniferous forest returned (the second *Conifer-period*).

The impoverishment of the forest-growth increased; finally in zone VIII, XII, XV only few *Betula*-pollengrains are present, together with chiefly *Pinus*-pollen. Possibly, the *Pinus*-forests were not so pronounced as the high frequency of *Pinus*-pollen would make suppose. Perhaps an almost treeless vegetation reigned, built up by mosses, *Ericaceae* and ferns, the *Pinus*-pollen being transported by the wind from far away to these countries.

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